Vacuum ultraviolet and infrared spectra of condensed methyl acetate on cold astrochemical dust analogs

Vacuum Ultraviolet and Infrared Spectra of Condensed Methyl Acetate on Cold Astrochemical Dust Analogs

B. Sivaraman[a,*], B. G. Nair[b], J. -I. Lo[c], S. Kundu[d], D. Davis[d], V. Prabhudesai[d], B. N. Raja Sekhar[e], N. J. Mason[b], B. -M. Cheng[c], E. Krishnakumar[d]

[a]*Space and Atmospheric Sciences Division, Physical Research Laboratory, Ahmedabad, India, 380009.*

[b]*Department of Physical Sciences, The Open University, Walton Hall, Milton Keynes, UK, MK7 6AA.*

[c]*National Synchrotron Radiation Research Center, 101 Hsinchu-Ann Road, Hsinchu Science Park, Hsinchu 30076, Taiwan.*

[d]*Department of Nuclear and Atomic Physics, Tata Institute of Fundamental Research, Mumbai, India, 400005.*

[e]*B-4, Indus-1, BARC Spectroscopy Lab at Indus-1, Atomic and Molecular Physics Division, BARC, Mumbai & RRCAT, Indore, India, 452 013.*

* corresponding author; email: bhala@prl.res.in

Abstract

Following the recent report of the first identification of methyl acetate (CH_3COOCH_3) in the interstellar medium (ISM) we have carried out Vacuum UltraViolet (VUV) and InfraRed (IR) spectroscopy studies on methyl acetate from 10 K until sublimation in an ultrahigh vacuum (UHV) chamber simulating astrochemical conditions. We present the first VUV and IR spectra of methyl acetate relevant to ISM conditions. Spectral signatures clearly showed molecular reorientation to have started in the ice by annealing the amorphous ice formed at 10 K. An irreversible phase change from amorphous to crystalline methyl acetate ice was found to be between 110 K and 120 K.

Keywords: *astrochemistry; ISM:molecules; methods:laboratory:solid state; technique: spectroscopic*

1. Introduction

The first identification of methyl acetate, CH_3COOCH_3, in the ISM was reported very recently (Tercero et al. 2013) using the IRAM 30-m radio telescope to explore the Orion constellation. Methyl acetate is considered to be the most abundant non cyclic isomer of $C_3H_6O_2$ other isomers of which (e.g. ethyl formate) having been detected and widely reported. Such compounds are postulated to form within the ice layers on ISM dust grains. Such formation mechanisms are expected to be similar to those synthesizing methyl formate, acetic acid and methanol. Based on the gas grain warm-up chemical model (Garrod, Weaver, & Herbst 2008) the reaction between CH_3O and CH_3CO radicals could lead to the formation of methyl acetate (Equation 1) in star forming regions. Current Laboratory based experiments may explore such routes of formation but such experiments require spectroscopic data if methyl acetate is to be identified in the solid ice phase. However, to date no VUV and IR spectroscopic data are available for methyl acetate in the ice phase at temperatures commensurate with the ISM. Accordingly we have measured, for the first time, VUV and IR spectra of methyl acetate ices using laboratory simulations of ISM dust grain ice analogs.

$$CH_3O + CH_3CO \rightarrow CH_3COOCH_3 \qquad (1)$$

2. Experimental procedure:

The VUV spectra of methyl acetate were measured using the National Synchrotron Radiation Research Center (NSRRC), Taiwan. VUV photons from the beamline were focused on a lithium fluoride (LiF) window, kept at 10 K, enclosed in a vacuum chamber at pressures of the order of 10^{-8} mbar. Further details on the experimental setup can be found in our earlier publication (Lu et al. 2008). The vapour from a liquid sample of methyl acetate

(99.5%, Sigma Aldrich) was allowed to form a uniform film of methyl acetate on a LiF substrate. Spectra (107 – 240 nm; 11.6 – 5.2 eV) were accumulated before and after deposition to obtain the incident (I_o) and transmitted (I_t) intensities from which absorbance spectra of the ice films were derived are calculated, using the Beer-Lambert law. The temperature dependence of the VUV spectra were recorded by annealing the sample to higher temperatures, which include 30 K, 75 K, 90 K, 100 K, 120 K, and 130 K. From 130 K temperature was brought back to 10 K to record a spectrum and then later the sample was warmed back to 130 K, 140 K and 150 K with subsequent recording of spectra. The minimum wavelength cut off (107 nm) in these spectra was determined by the window material used (LiF) as both the entrance and substrate window.

The IR spectra reported in this paper were all carried out in a new experimental setup (Figure 1) that was designed and developed at the Tata Institute of Fundamental Research (TIFR), India, to study molecules in the condensed phase using Fourier Transform InfraRed (FTIR) spectroscopy. The main components of the experimental chamber were a cold head (closed cycle helium cryostat) with a sample mount that can reach temperatures down to 12 K whilst the chamber pressure was of the order of 10^{-10}mbar (obtained using the combination of turbo and dry backing pumps). Molecules were condensed onto a gold substrate attached to the sample mount with the temperature at the substrate controlled using a combination of Si diode sensor and UHV heater looped to a temperature controller.

By introducing methyl acetate (99.5%, Sigma Aldrich) vapours into the UHV chamber and subsequent recording of mid-IR spectra (4000-800 cm^{-1}), molecules of methyl acetate were found to condense on the gold substrate at 15 K. After deposition at 15 K the ice was then warmed up in 10 K steps up to 95 K and to further higher temperatures at 5 K steps until 130 K. After reaching 130 K sample was then cooled back 15 K to record an IR spectrum and then the ice was annealed in 10 K steps until sublimation.

3. Results

The VUV spectrum recorded at 10 K was found to have strong absorption from 107 nm – 180 nm (11.6 – 6.9 eV) with three distinct peaks at 134 nm, 152 nm and 165 nm (Figure 2a). A spectrum recorded at 30 K, was found to be similar to the spectrum at 10 K. However by further increasing the temperature to 75 K the spectrum was found to develop as one broad peak (peak centre ~146 nm) containing vibronic structures in the 131 – 160 nm region. This region was observed to gain intensity whilst the fine structure was also found to be more profound in the spectrum recorded at 100 K. At 120 K, the peak in the 131 – 160 nm region intensified and also shifted to ~ 142 nm whereas the fine structure was found to diminish and then smoothened at 130 K (Figure 2a). The sample was then cooled back down to 10 K and the spectrum recorded was found to be similar to the spectrum recorded at 130 K before cooling down. Spectrum recorded at 150 K, by re-annealing the methyl acetate ice back to higher temperatures, was observed to be very less intense.

Infrared spectra of methyl acetate ice were recorded at various temperatures, between 15 K and 150 K. Spectra recorded at 15 K were found to contain several peaks (Figure 3), as listed in Table 1. Fundamental vibrations were observed in the spectral range 4000 – 800 cm^{-1} including features at 3021.5 cm^{-1} (ν_1), 2997.7 cm^{-1} (ν_2), 2942 cm^{-1} (ν_3), 2957.3 cm^{-1} (ν_4), 1735.7cm^{-1} (ν_5), 1464.5 cm^{-1} (ν_6), 1439.5 cm^{-1} (ν_8), 1368.7 cm^{-1} (ν_9), 1246.2 cm^{-1} (ν_{10}), 1191.7 cm^{-1} (ν_{11}), 1044 cm^{-1} (ν_{12}), 977.2 cm^{-1} (ν_{13}) and 849 cm^{-1} (ν_{14}) attributed to (C)CH_3 stretch, (O)CH_3 stretch, (C)CH_3 stretch, (O)CH_3 stretch, C=O stretch, (O)CH_3 bending,(O)CH_3 asymmetric bending,(C)CH_3 bending, skeletal deformation, (O)CH_3 rocking, O-CH_3 stretch, (C)CH_3 rocking and skeletal deformation, respectively. The bands at ν_{10} and ν_{14} are assigned to C-O stretching and H_3C-C stretching vibrations, respectively, by Fausto & Teixeira-Dias (1986) and Wilmshurst (1957). However, the same bands at ν_{10} and ν_{14} are assigned to C- O stretching vibration by Zahidi et al (1994). Band positions and their assignments are given in

Table 1. The fundamental CH_3 bending vibration at ν_7 was not observed, in the spectra at 15 K after deposition of the ice, explicitly due to the band overlap from ν_6 and ν_8. Apart the fundamental vibrations an overtone of the C=O vibration at 3460.2 cm^{-1} ($2\nu_5$; Figure 2b), an overtone of (O)CH_3 bending vibration at 2907.2 cm^{-1} ($2\nu_6$), an overtone of (O)CH_3 asymmetric bending at 2848.7 cm^{-1} ($2\nu_8$), an overtone of O-CH_3 stretch at 2093.6 cm^{-1} ($2\nu_{12}$), an overtone of (C)CH_3 rocking at 1955 cm^{-1} ($2\nu_{13}$) and an overtone of the skeletal deformation at 1707.8 cm^{-1} ($2\nu_{14}$) were also observed. About four combination bands were also observed at 2717.7 cm^{-1} ($\nu_5+\nu_{13}$), 2589.6 cm^{-1} ($\nu_5+\nu_{14}$), 2223.9 cm^{-1} ($\nu_9+\nu_{14}$) and 1897.3 cm^{-1} ($\nu_{12}+\nu_{14}$).The rest of the bands observed, as listed in Table 1, corresponds to a group of combination and overtone bands of those fundamental vibrations observed. These unassigned bands may be due to the combination and overtone bands of those fundamental peaks beyond 800 cm^{-1}.

Upon warming the IR spectra to higher temperatures significant changes in band position and spectral shape were observed (Figure 3). At 120 K the $2\nu_5$ band was observed at 3438.7 cm^{-1} having shifted by ~22 cm^{-1} with respect to the spectra recorded at 15 K. However, the fundamental vibration corresponding to CO stretch (ν_5) shifted by only ~ 7 cm^{-1}. The rest of the bands corresponding to the fundamental vibrations were also observed to have shifted (refer Table 1) and at this temperature (120 K) aband at 1447.4 cm^{-1}, corresponding to (C)CH_3 asymmetric bending (ν_7), appeared along with the other two bands ν_6 andν_8. Several other new bands appeared in the spectra at 2498.6 cm^{-1},2427.7 cm^{-1}, 1272$cm^{-1}$and these are assigned to $2\nu_{10}$, $\nu_8+\nu_{13}$, ν_{10}, respectively, the remaining new bands that appeared at 1381.7 cm^{-1}, 1126.7 cm^{-1}, 1055 $cm^{-1}$and 1036.8 cm^{-1} are currently left unassigned (Figure 3; Table 1). Before such a big change observed in the IR spectra at 120 K, only the peak position of the $2\nu_5$ (overtone of the C=O) band was observed to gradually shift by about ~ 5 cm^{-1} (Figure 2b) for increase in temperature from 15 K – 110 K.

After heating the sample to 120 K, the temperature of the substrate was brought back to 15 K. The spectrum of this 'annealed ice' was found to contain seven new bands at 3022 cm^{-1}, 2987.9 cm^{-1}, 2738.9 cm^{-1}, 2490.5 cm^{-1}, 1984.2 cm^{-1}, 1844.2 cm^{-1}and1457.2 cm^{-1} (Figure 3).While most of these new bands are left unassigned, the 1457.2 cm^{-1} band may correspond to the (O)CH_3 bending vibration (Senent et al. 2013). However, the fundamental, overtone and combination bands that were discussed earlier for the methyl acetate ice at 15 K and 120 K were also observed to have shifted by few cm^{-1} (Figure 3) by recooling the sample to 15 K. Upon annealing the methyl acetate ice back to 130 K from 15 K the spectra was found be identical to the spectra that was recorded at 130 K before cooling down. Upon further heating the band intensities were found to diminish above 140 K and a spectrum recorded at 150 K had no IR signatures of methyl acetate showing that the sublimation temperature for methyl acetate under these (ISM) conditions lie between 140 and 150K.

4. Discussion

Upon warming the ice to higher temperatures spectral changes in the VUV spectra at 120 K clearly suggest a phase change to occur in the ice. At 120 K, significant changes in the peak position and intensity together with the diminishing vibrational signature (Figure 4) could be due to the change in morphology of the ice from amorphous to crystalline. IR spectra of methyl acetate ice recorded at 15 K and 120 K also reveal significant changes in band peak positions and shapes (Figure 4) confirming the phase change from amorphous to crystalline to have occurred in the ice. However, the phase change temperature could be between 110 K and 120 K because the spectra recorded at 120 K was observed to show a phase change that had completed and the spectrum at 110 K was found to match with the spectra of the amorphous ice at lower temperatures. Transformation from ***cis*** to ***trans*** conformer of methyl acetate by annealing cannot happen due to the large barrier 4457 cm^{-1} (Senent, et al. 2013) involved in this transformation. Also the band positions for ***trans***-methyl acetate calculated in

Senent et al (2013) were not observed. Therefore by comparing the VUV and IR spectra recorded at different temperatures we notice that the ice formed at 10 K was amorphous ***cis***-methyl acetate ice.

From the VUV spectra recorded by recooling the sample to 10 K from 130 K the phase change from amorphous to crystalline form was found to be irreversible. However, the new bands that were observed in the IR spectra (Figure 3) recorded at 15 K, after re-cooling, was an effect of temperature since the spectra recorded by reheating back to 130 K was found to be similar to the spectra obtained at 130 K before recooling. Therefore, those spectra obtained at 10 K and 15 K, by recooling the crystalline sample, were indeed the crystalline VUV and IR spectra of methyl acetate ice at lower temperatures, respectively. The intensity variation of the spectra recorded at even higher temperatures indicates that the methyl acetate ice sublimes above 140 K and below 150 K.

New structures observed in the 131 nm – 160 nm region of the VUV spectra recorded from 75 K – 110 K (Figure 2a), and the observed gradual shift in the $2\nu_5$ (overtone of the C=O) vibrational mode peak position by about ~ 5 cm^{-1} (Figure 2b) in the IR spectra from 15 K – 110 K, just before phase change, might correspond to the reorientation of molecules altering the density of the ice upon annealing.Such rearrangement before crystallisation may have an effect on the mobility of atoms or molecules that may be trapped in methyl acetate ices, exposed to irradiation.

5. Conclusion and implications

VUV and IR spectra of methyl acetate were recorded over a range of temperatures, from which we conclude that upon deposition at lower temperatures methyl acetate forms an

amorphous ice which, by annealing, changes irreversibly to a crystalline form at temperature between 110 K to 120 K. VUV and IR spectra clearly showed the rearrangement of methyl acetate molecules within the ice well before crystallisation. Our spectra can be used to identify and interpret the morphology of methyl acetate ices in different regions of the ISM. Also from the sublimation temperature of methyl acetate ices we can understand that it can sustain and contribute to chemical changes in the icy mantles of dust grains until 140 K. Future laboratory simulation experiments will therefore focus on the formation of methyl acetate molecules in the ice phase by charged particle irradiation.

Acknowledgements

BS would like to acknowledge the beamtime grant from NSRRC, Taiwan and DST Inspire grant number IFA-11CH-11. NJM acknowledges support from the EU FP7 programme LASSIE LABORATORY ASTROCHEMICAL SURFACE SCIENCE IN EUROPE, Grant Agreement 238258.

Figures

Figure 1: Schematic of the experimental arrangement, simulating the ISM dust grain ice analog, used to form pure methyl acetate ice and to record IR spectra.

Figure 2: [a] VUV spectra of methyl acetate ice as a function of temperature. [b] IR spectra of pure methyl acetate ice in the $2\nu_5$ region, before phase transition. Please note the spectra are shifted upward for clarity.

Figure 3: IR spectra of pure ***cis***-methyl acetate ice at 15 K (amorphous), 120 K (crystalline) and recooled to 15 K (crystalline). For band positions and assignments refer Table 1. Please note the spectra are shifted upward for clarity.

Figure 4: VUV and IR spectra of amorphous and crystalline pure methyl acetate ices. The IR spectrum is shifted for clarity.

Table 1: Observed peak positions in the infrared spectra of pure ***cis***-methyl acetate ice at different temperatures.

15 K (amorphous)	120 K (crystalline)	15 K (crystalline)	Mode	Assignment	Reference
3460.2	3438.7	3435.2	$2\nu_5$	Overtone of C=O vibration	
		3418.7			
3021.5	3029.8	3031.2	ν_1	(C)CH3 stretch	1
		3022			
2997.7	3001.8	3001.4	ν_2	(O)CH3 stretch	1
		2987.9			
2957.3	2957	2958.6	ν_4	(O)CH3 stretch	1
2942	2942	2940.8	ν_3	(C)CH3 stretch	1
2907.2	2912.2		$2\nu_6$	Overtone of (O)CH3 bending	
2848.7	2845	2844.8	$2\nu_8$	Overtone of (O)CH3 asymmetric bending	
2825.5	2831				
		2738.9			
2717.7		2713.7	$\nu_5+\nu_{13}$	Combination band	
2589.6			$\nu_5+\nu_{14}$	Combination band	
	2498.6	2500.9	$2\nu_{10}$		
		2490.5			
	2427.7	2430.1	$\nu_8+\nu_{13}$	Combination band	
2223.9	2230.4	2230.1	$\nu_9+\nu_{14}$	Combination band	
2093.6	2100	2100.8	$2\nu_{12}$	Overtone of O-CH3 stretch	
	2034.9	2035.32	$\nu_{11}+\nu_{14}$	Combination band	
2019.2	2019.5				
		1984.2			
1955	1978.3	1978.9	$2\nu_{13}$	Overtone of (C)CH3 rocking	
1897.3	1898.9	1899.9	$\nu_{12}+\nu_{14}$	Combination band	
		1844.2	$\nu_{13}+\nu_{14}$	Combination band	
1735.7	1728.5	1725.5	ν_5	C=O stretch	1,2
1707.8	1701	1700.7	$2\nu_{14}$	Overtone	
	1683.3	1679.2			
1663.9		1653.4			
1623.6	1630.7	1634.5			
1491.3	1491.5	1495			
1464.5	1467.5	1469.3	ν_6	(O)CH3 bending	1
		1457.2	ν_6?	(O)CH3 bending	1

	1447.4	1448.7	ν_7	(C)CH3 asymmetric bending	2
1439.5		1439.3	ν_8	(O)CH3 symmetric bending	2
	1381.7	1381.4			
1368.7	1364.6	1364.6	ν_9	(C)CH3 bending	1
1283.7	1279.4	1289.9			
	1272	1278.4	ν_{10}	C-O stretch	2
1246.2	1240	1239.6	ν_{10}	Skeletal deformation*	1
1228	1230.2	1232.1			
1191.7	1185	1185.9	ν_{11}	(O)CH3 rocking	1
1158.3	1160.5	1160.3			
1137.3	1138.8	1138			
	1126.77	1126.4			
1088.6	1088.2	1088.5			
	1055	1056.3			
1044	1047.6	1048	ν_{12}	O-CH3 stretch	1
	1036.8	1036.4			
977.2	988.7	990.2	ν_{13}	(C)CH3 rocking	1
849	852.3	853.2	ν_{14}	Skeletal deformation*	1

Band positions for ***trans***-methyl acetate given in Senent et al (2013) were not observed. ^ $2\nu_{10}$ is an overtone of the ν_{10} band assigned to the skeletal deformation. References:[1](Senent, et al. 2013) and [2](Zahidi, Castonguay, & McBreen 1994).

References

Garrod, R. T., Weaver, S. L. W., & Herbst, E. 2008, The Astrophysical Journal, 682, 283

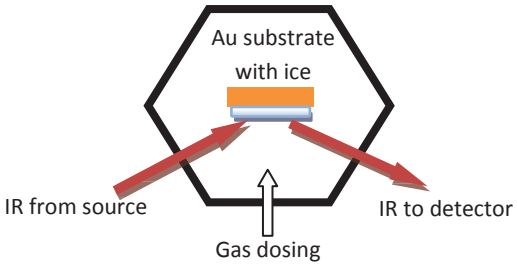
Lu, H.-C., Chen, H.-K., Cheng, B.-M., & Ogilvie, J. F. 2008, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 71, 1485

Senent, M. L., Domínguez-Gómez, R., Carvajal, M., & Kleiner, I. 2013, Journal of Chemical Physics, 138, 044319

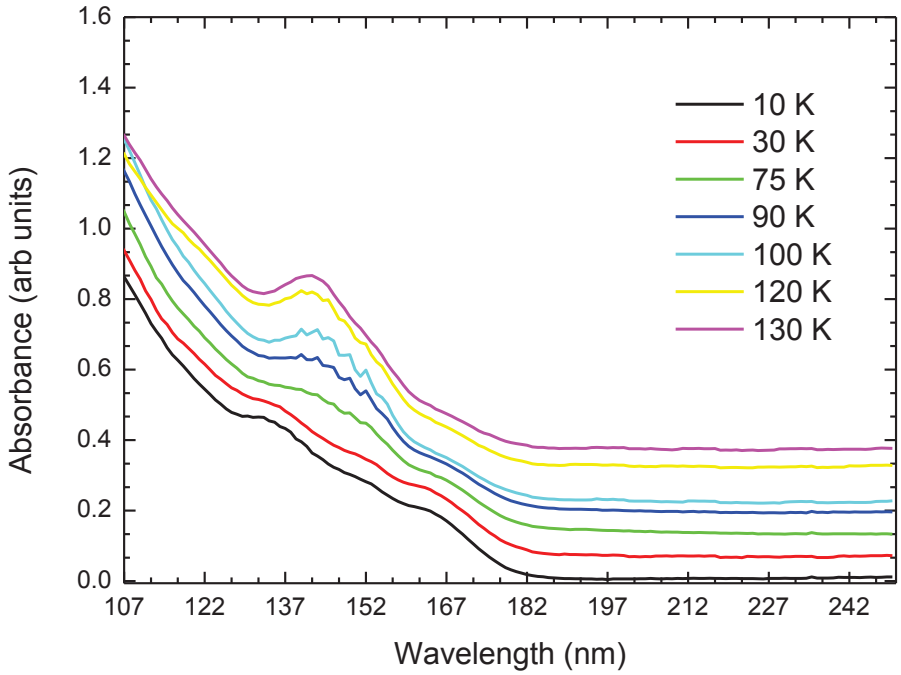
Tercero, B., Kleiner, I., Cernicharo, J., Nguyen, H. V. L., Lopez, A., & Caro, G. M. M. 2013, The Astrophysical Journal Letters, 770, 6pp

Wilmshurst, J. K. 1957, Journal of Molecular Spectroscopy, 1, 201

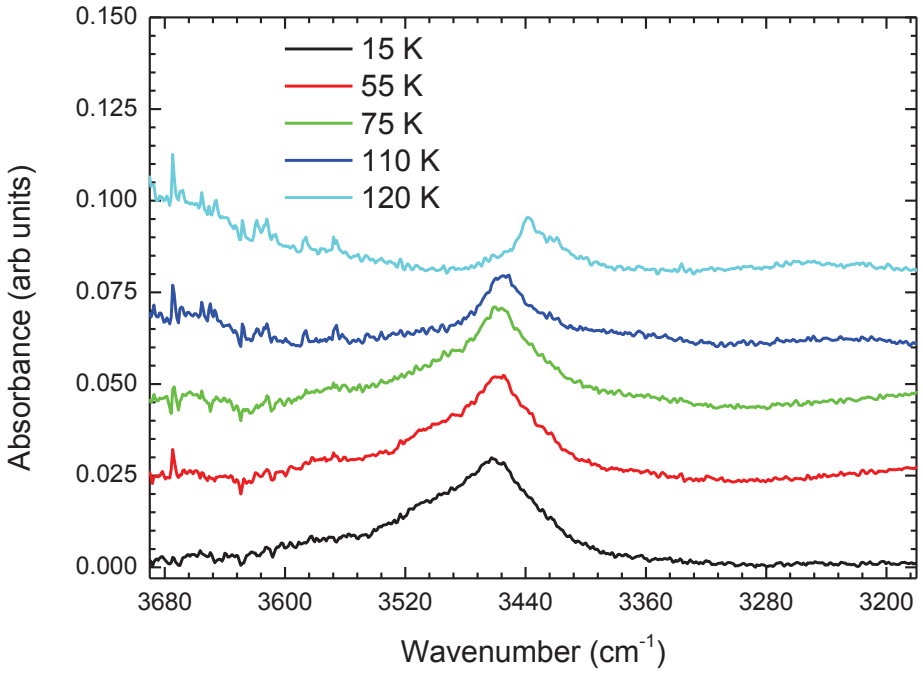
Zahidi, E., Castonguay, M., & McBreen, P. 1994, Journal of American Chemical Society, 116, 5847

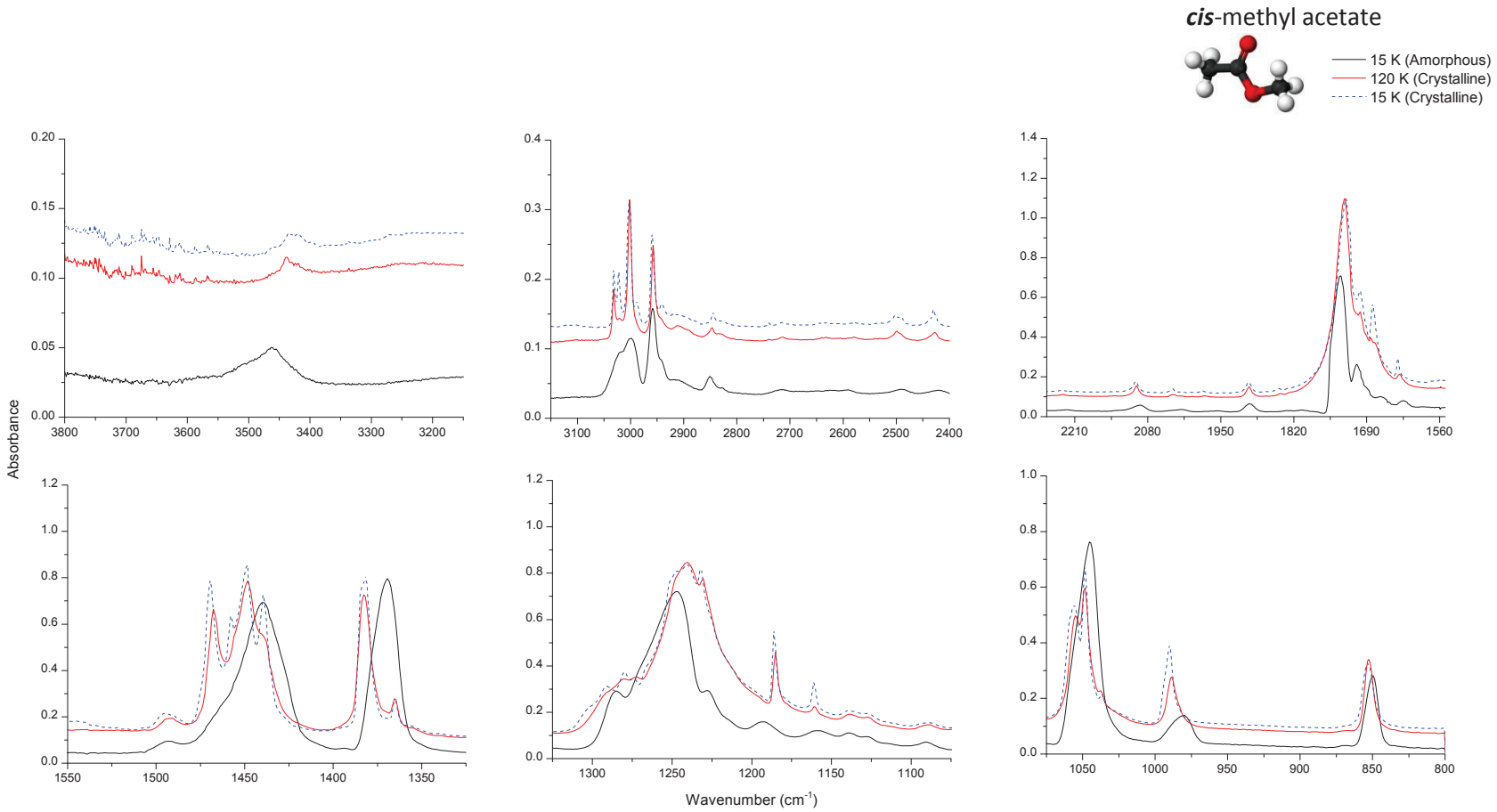

Au substrate
with ice
IR from source
IR to detector
Gas dosing

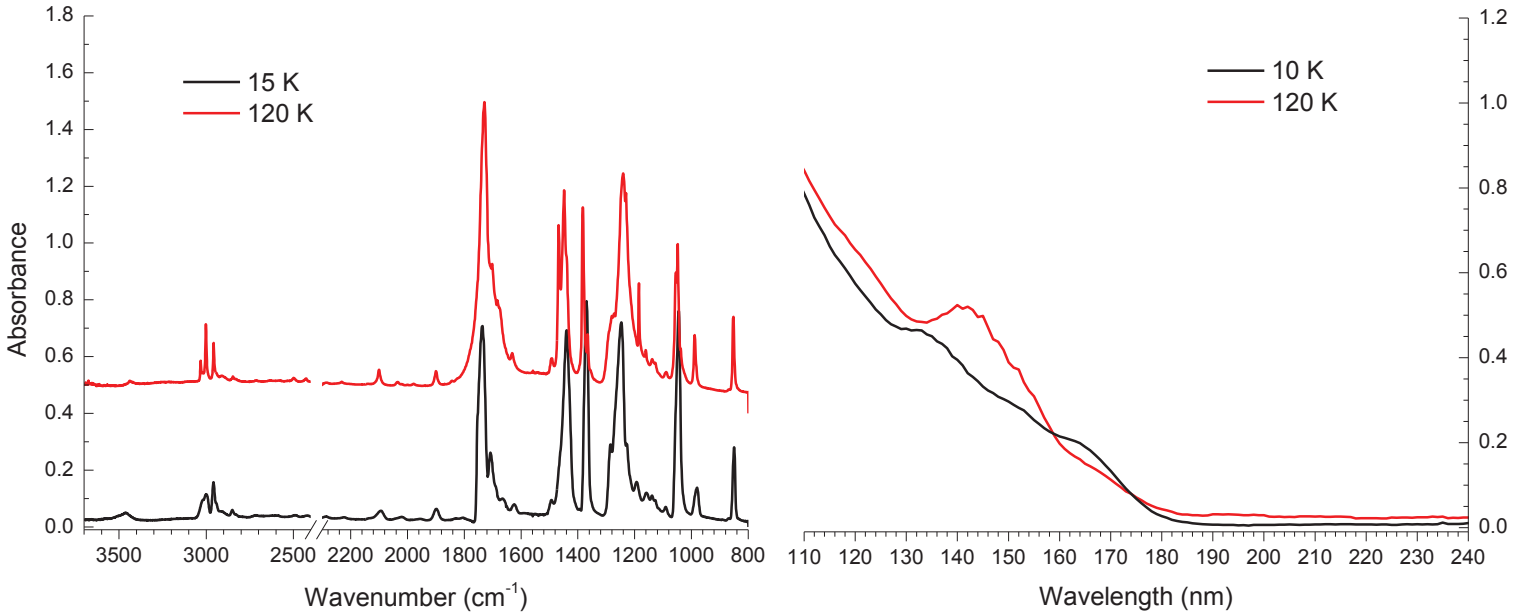
[a]


Absorbance (arb units)
Wavelength (nm)
10 K
30 K
75 K
90 K
100 K
120 K
130 K
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
107
122
137
152
167
182
197
212
227
242

[b]


Absorbance (arb units)
Wavenumber (cm-1)
15 K
55 K
75 K
110 K
120 K
0.000
0.025
0.050
0.075
0.100
0.125
0.150
3680
3600
3520
3440
3360
3280
3200


cis-methyl acetate
15 K (Amorphous)
120 K (Crystalline)
15 K (Crystalline)
Absorbance
Wavenumber (cm-1)


15 K
120 K
Absorbance
Wavenumber (cm-1)
10 K
120 K
Wavelength (nm)